

1,155,927



# PATENT SPECIFICATION

## DRAWINGS ATTACHED

1,155,927

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### COMPLETE SPECIFICATION

#### Electrolytic manufacture of alkali metals.

We, IMPERIAL CHEMICAL INDUSTRIES LIMITED of Imperial Chemical House, Millbank, London S.W.1, a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to the manufacture of alkali metals. More particularly it relates to an electrochemical method for the extraction of alkali metals from alkali metal amalgams and to apparatus therefor.

The established manufacture of the alkali metals is best illustrated by the manufacture of sodium. The most widely used industrial process for the manufacture of metallic sodium involves the electrolysis of a molten electrolyte containing sodium chloride. This process has the disadvantages of a high operating temperature, approaching 600°C, which leads to frequent damage of the cell components, and also a high energy consumption, owing to a current efficiency of sodium production appreciably lower than 100% and a high overall cell voltage, which is mainly due to the resistance of the electrolyte in the wide gap that has to be maintained between the electrodes. In the mercury cell process for the electrolysis of aqueous solutions of sodium chloride, the sodium amalgam produced at the cathode is obtained at much higher current efficiency and with a much lower overall cell voltage.

The attraction of extracting sodium from this amalgam if it could be done with a small expenditure of energy has long been realised and several methods have been proposed for isolating metallic sodium from this source. Thus at various times it has been proposed to recover the sodium from sodium amalgam by distilling out the large proportion of mercury or by an electrolytic method in which the amalgam is made the anode of a cell with a fused salt or a non-

aqueous solution as electrolyte and sodium is liberated at a cathode. Various electrolytes have been proposed, e.g. fused caustic soda or lower-melting mixtures of the hydroxide and halides of sodium, particularly sodium iodide, which yield free metallic sodium directly, and solutions of sodium cyanide in liquid ammonia which yield the sodium in the form of a solution in liquid ammonia as a separate layer in the electrolyte and containing only a small proportion of cyanide, from which sodium can be obtained by evaporation of the ammonia. Such processes are described in British Patent Specifications No. 218,373, No. 491,879, No. 491,880 and No. 505,212. All these processes are difficult to operate and suffer from the disadvantages of leaving the product contaminated with mercury and/or electrolyte or in requiring the use of toxic chemicals, refrigeration or elevated pressure working.

The present invention provides a method of extracting an alkali metal in a highly pure state from an alkali metal amalgam by an electrochemical process which involves a minimum expenditure of energy. The invention is considered to be of the greatest industrial importance when applied to the extraction of sodium and potassium from their respective amalgams.

According to the present invention, we provide a method of extracting an alkali metal from an alkali metal amalgam which comprises passing an electrolysis current through a concentration cell wherein the alkali metal amalgam is made anodic, the cathode is the same alkali metal in the liquid state and the electrolyte is a polycrystalline ceramic material which is permeable only to monovalent cations.

In a preferred embodiment of the invention in accordance with the preceding paragraph a stream of alkali metal amalgam is supplied continuously to an anode com-

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am 10. JULI 1997  
Erledigt  
Patentschriftensammlung

partment in contact with the solid electrolyte, a stream of the alkali metal amalgam of lower alkali metal content is continuously removed from the anode compartment and a stream of the liquid alkali metal is continuously removed from a cathode compartment in contact with the solid electrolyte.

Suitable polycrystalline ceramic materials for use as the solid electrolyte are in organic materials having a crystal lattice structure which contains a large number of defects and containing sodium ions or other monovalent cations capable of replacement by alkali metal ions. The number of defects must not, however, be so large as to render the material an electronic conductor. One very suitable material, particularly when the alkali metal to be extracted from its amalgam is sodium, is that known as beta-alumina. This has the approximate composition  $\text{Na}_2\text{O} \cdot 11\text{Al}_2\text{O}_3$ , and the sodium ions in the crystal lattice can exchange with alkali metal ions introduced from outside. Other suitable materials are certain aluminates, aluminosilicates and titanates.

The invention also includes within its scope an electrolytic cell for the extraction of an alkali metal from an alkali metal amalgam which comprises at least one anode chamber and at least one cathode chamber, each anode chamber being in juxtaposition with at least one cathode chamber and being separated therefrom over at least part of the common boundary therewith only by a solid electrolyte in the form of a wall of polycrystalline ceramic material which is permeable only to monovalent cations, each anode chamber being substantially filled with liquid alkali metal amalgam and having an inlet and an outlet therefor, each cathode chamber being substantially filled with the same alkali metal and having an outlet for liquid alkali metal, electrical connection means for connecting the alkali metal amalgam in each anode chamber to the positive pole of a direct current source and electrical connection means for connecting the alkali metal in each cathode chamber to the negative pole of this direct current source.

Three embodiments of cells according to the invention are shown in the schematic drawings accompanying the Provisional Specification, which are not to scale. In its most preferred form the invention is applied to the extraction of sodium from a sodium amalgam. For the sake of brevity the drawings will therefore be discussed with reference to the extraction of sodium. It should however be understood that the invention is not limited thereto but that the references to sodium and sodium amalgams are replaceable in the text by reference to another alkali metal and its respective amalgams.

Fig. 1 represents in elevation a section through a cell containing one anode chamber and one cathode chamber.

Fig. 2 indicates a general arrangement in which anode and cathode chambers alternate side by side in a multi-chamber cell.

Fig. 3 represents in elevation a section through a form of cell in which two cathode chambers are enclosed within a common anode chamber, and Fig. 4 is a plan view taken along the line A-A of Fig. 3.

In Fig. 1 an anode chamber 1 is bounded by a casing 2, suitably of mild steel, in the form of a box having one open side which is closed by a sheet of polycrystalline ceramic material which is permeable only to monovalent cations, e.g. beta-alumina 3, suitably about 0.5 cm. thick. 4 is a cathode chamber which is bounded by a casing 5 similar to the casing 2 and which also has its one open side closed by sheet 3. 2, 3 and 5 are held together in liquid-tight manner by means of clamps (not shown), with sealing means 6 interposed between sheet 3 and the edges of boxes 2 and 5. Anode chamber 1 is filled with sodium amalgam and cathode chamber 4 is filled with sodium. Pipe 7 serves for introducing a sodium amalgam stream into anode chamber 1 and pipe 8 serves for removing sodium amalgam therefrom. Pipe 9 serves to remove liquid sodium product from cathode chamber 4 and will generally be connected to another vessel (not shown) for collection of sodium. 10 and 11 are electrical conductors fixed to anode box 2 and cathode box 5 respectively for applying an external electrical potential between the sodium amalgam in chamber 1 and the sodium in chamber 4.

In the cell arrangement of Fig. 2, the end chambers 1 and 4 are an anode and a cathode chamber respectively corresponding to the same numbered parts in Fig. 1. Between these two chambers are a cathode chamber 12 and an anode chamber 13 so that in the whole arrangement anode and cathode chambers alternate with each other. Each chamber is separated from the next chamber by a sheet of polycrystalline ceramic material which is permeable only to monovalent cations, e.g. beta-alumina 3, and chambers 12 and 13 are enclosed on their other four sides by mild steel box structures 14 and 15 respectively. The whole arrangement of chambers is held together in liquid-tight manner by means of clamps (not shown), with sealing means 6 interposed between the edges of each mild steel unit and the juxtaposed sheets 3. Anode chambers 1 and 13 are filled with sodium amalgam and cathode chambers 4 and 12 are filled with sodium. Chambers 1 and 13 are each provided with an inlet and an outlet for a stream of sodium amalgam, and chambers

4 and 12 are each provided with an outlet for liquid sodium. These inlets and outlets have been omitted from the drawing for the sake of clarity. 16 and 17 are electrical connection means passing in liquid-tight manner through the steel casings of chambers 1 and 13 and joined together as shown for making electrical connection between the sodium amalgam in these two chambers in parallel and the positive pole of a direct current source. 18 and 19 are similarly-arranged connecting means for making electrical connection between the negative pole of the same direct current source and the sodium in chambers 4 and 12. It should be understood that, although only one pair of cathode and anode chambers 12 and 13 is shown in the drawing, any number of such pairs with their ancillary connections may be placed between the end chambers 1 and 4 to provide an alternating sequence of anode and cathode chambers.

In the cell arrangement of Fig. 3 and Fig. 4 there is a single anode chamber 20 bounded by a mild steel container 21. 22 is an inlet for a stream of sodium amalgam, and 23 is an overflow outlet for spent amalgam so that chamber 20 is substantially filled with amalgam as shown. Two cathode chambers 24 are each formed from cylindrical side walls 25 of polycrystalline ceramic material which is permeable only to monovalent cations, e.g. beta-alumina, a circular base 26 and a circular cover 27, which are held together in liquid-tight manner with clamps (not shown). The covers 27 are made of electrically insulating material. The bases 26 may be of insulating material or, if desired, they may be made of beta-alumina like the side walls 25. Each cathode chamber is inserted into the anode chamber through a circular hole in the cover of the container 21 and is held in position by bolts 28 through the outer edges of its cover 27. Cathode chambers 24 are filled with sodium and are connected by pipes 29 to pipe 30, which is an outlet for liquid sodium. 31 and 32 are electrical connection means passing in liquid-tight manner through covers 27 for making electrical connection between the sodium in cathode compartments 24 and the negative pole of a direct current source as indicated at 33. 34 is a current lead attached to the underside of container 21 for making electrical connection between the sodium amalgam in anode compartment 20 and the positive pole of the direct current source through the conducting casing 21. Although only two cathode compartments 24 are shown in Fig. 3 and Fig. 4, any number of such cathode compartments may be placed within one anode compartment. Alternatively a very compact unit cell may be made by placing a single cylindrical cathode compartment of this type within a

coaxial anode compartment, i.e. an anode compartment having cylindrical retaining walls. It will also be readily understood that with these cell arrangements in which one or more cathode compartments have been shown as immersed in an anode compartment the function of the two varieties of electrode compartment can be reversed if desired, i.e. each inner compartment can be filled with sodium amalgam and provided with feed and discharge pipes therefor, and the outer compartment can be filled with liquid sodium and provided with an outlet therefor, so that by reversing the connections to the electrolysing current source a cathode compartment surrounds each anode compartment and the sodium metal produced travels outwards instead of inwards during operation of the cell.

In carrying out the method of the invention for the extraction of sodium the sodium in the cathode compartments of the cell must be maintained in the liquid state. Furthermore, in order to reduce the ohmic resistance of the cell it is preferred to work at as high a temperature as convenient. Since it is undesirable to approach the boiling point of mercury (359°C) a maximum operating temperature of about 300°C is most convenient.

A stream of sodium amalgam is fed to the anode compartments of the cell, usually from a mercury-cathode cell electrolysing sodium chloride brine, and containing for example 0.2-0.4% by weight of sodium, and spent amalgam of lower sodium content, for instance 0.05% by weight, is continuously withdrawn from the anode compartments. When the sodium cell is fed with amalgam from a mercury-cathode cell an interrupter may be inserted to break the continuity of the amalgam stream so as to isolate the two cells electrically from each other if desired. Since mercury-cathode cells operate at comparatively low temperature, the amalgam stream is preferably heated before it enters the sodium cell. If the spent amalgam is returned direct to the mercury-cathode cell, the two amalgam streams may conveniently be passed through a heat exchanger so as to heat the amalgam stream entering the sodium cell while cooling the return stream to the mercury-cathode cell and thereby conserving heat. With this arrangement, and depending on design of the sodium cell, the additional heating effect of the electrolysing current may be sufficient to maintain the desired temperature in the sodium cell. If additional heating of the sodium cell is required, this can be supplied from an external source, for instance by means of a heating jacket.

In a sodium cell according to the invention the current is carried by sodium ions which are driven through the solid electro-

lyte by the electrolysing potential applied between the anode and cathode chambers. Sodium is therefore transferred to the cathode chambers in a pure state, since the solid electrolyte behaves as a barrier to mercury and mercury ions. Since the ohmic resistance of the cell is quite low it is necessary to apply only a low voltage to overcome the reversible voltage of the sodium concentration cell and the small ohmic resistance. Thus for a current density of 5 kA/in<sup>2</sup> of solid electrolyte area between the anode and cathode chambers the overall cell voltage is only about 1.1-1.2 volts.

The invention is further illustrated by the following example of the extraction of sodium from a sodium amalgam.

#### EXAMPLE

A laboratory-scale electrolysis cell was set up which was equivalent to one unit cell of Fig. 4. The cathode chamber was in the form of a crucible of beta-alumina so that the side walls and base were of beta-alumina. The anode chamber was constituted by a glass vessel with an open top neck. A long glass tube was connected to the neck of the anode chamber and a ceramic tube was sealed to the rim of the beta-alumina crucible so that the surface of the sodium and the sodium amalgam placed in the cathode and anode chambers respectively could be blanketed by a flow of inert gas passed down the aforesaid glass and ceramic tubes through gas-feed tubes inserted therein. 10 g. of sodium were placed in the cathode chamber and this was inserted down the glass tube into the anode chamber and was immersed in 2 kg. of sodium amalgam placed therein and containing 0.36% by weight of sodium. Negative and positive conductors passing down the ceramic and glass tubes were introduced into the sodium cathode and the sodium amalgam anode respectively and the cell was heated in an oven to  $255 \pm 5^\circ\text{C}$ . Current from a D.C. source was passed through the cell by way of the aforesaid conductors and was measured at intervals. Sodium was thereby transferred through the solid beta-alumina electrolyte from the amalgam anode to augment the liquid sodium cathode and in a run of 165 minutes the current efficiency calculated from the weight of sodium transferred to the cathode chamber and the measured coulombic sum averaged 94.5%. At the end of the run the sodium in the cathode compartment contained not more than 1 p.p.m. mercury.

#### WHAT WE CLAIM IS:—

1. A method of extracting an alkali metal from an alkali metal amalgam, which comprises passing an electrolysing current through a concentration cell wherein the alkali metal amalgam is made anodic, the

cathode is the same alkali metal in the liquid state and the electrolyte is a polycrystalline ceramic material which is permeable only to monovalent cations.

2. A method according to Claim 1, wherein the polycrystalline ceramic material is beta-alumina.

3. A method according to either of the preceding claims, wherein a stream of alkali metal amalgam is supplied continuously to an anode chamber in contact with the polycrystalline ceramic material, a stream of the alkali metal amalgam of lower alkali metal content is continuously removed from the anode chamber and a stream of the alkali metal in the liquid state is continuously removed from a cathode chamber in contact with the polycrystalline ceramic material.

4. A method according to any of the preceding claims, wherein the alkali metal is sodium.

5. A method according to Claim 3 wherein the said stream of alkali metal amalgam supplied continuously to an anode chamber in contact with the polycrystalline ceramic material is an exit stream of sodium amalgam obtained from a cell electrolysing sodium chloride brine with a flowing mercury cathode.

6. A method according to Claim 3 wherein the said stream of the alkali metal amalgam of lower alkali metal content continuously removed from the said anode chamber is a stream of sodium amalgam and is employed as a feed to the flowing cathode of a mercury-cathode cell electrolysing sodium chloride brine.

7. An electrolytic cell for the extraction of an alkali metal from an alkali metal amalgam by a method as claimed in Claim 1, which comprises at least one anode chamber and at least one cathode chamber, each anode chamber being in juxtaposition with at least one cathode chamber and being separated therefrom over at least part of the common boundary therewith only by a solid electrolyte in the form of a wall of polycrystalline ceramic material which is permeable only to monovalent cations, each anode chamber being substantially filled with liquid alkali metal amalgam and having an inlet and an outlet therefor, each cathode chamber being substantially filled with the same alkali metal and having an outlet for liquid alkali metal, electrical connection means for connecting the alkali metal amalgam in each anode chamber to the positive pole of a direct current source and electrical connection means for connecting the alkali metal in each cathode chamber to the negative pole of this direct current source.

8. An electrolytic cell according to Claim 7 wherein the wall of polycrystalline

BAJF  
?

BAJF  
?

ceramic material consists of beta-alumina.

9. An electrolytic cell according to either of Claims 7 and 8, wherein each anode chamber is substantially filled with liquid sodium amalgam and each cathode chamber is substantially filled with sodium.

10. An electrolytic cell according to any of Claims 7-9, wherein an anode chamber and a cathode chamber are juxtaposed side by side and a flat sheet of the said polycrystalline ceramic material forms a common dividing wall therebetween.

11. An electrolytic cell according to any of Claims 7-9, wherein at least one cathode chamber is immersed in an anode chamber.

12. An electrolytic cell according to any of Claims 7-9, wherein at least one anode chamber is immersed in a cathode chamber.

13. An electrolytic cell for the extraction of an alkali metal from an alkali metal

amalgam substantially as hereinbefore described with reference to the drawings accompanying the Provisional Specification.

14. A method of extracting an alkali metal from an alkali metal amalgam as claimed in Claim 1 and substantially as hereinbefore described.

15. An alkali metal whenever produced by a method as claimed in any of Claims 1-6.

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Agent for the Applicants.

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2 SHEETS

PROVISIONAL SPECIFICATION

This drawing is a reproduction of  
the Original on a reduced scale.

SHEET 1

FIG.1

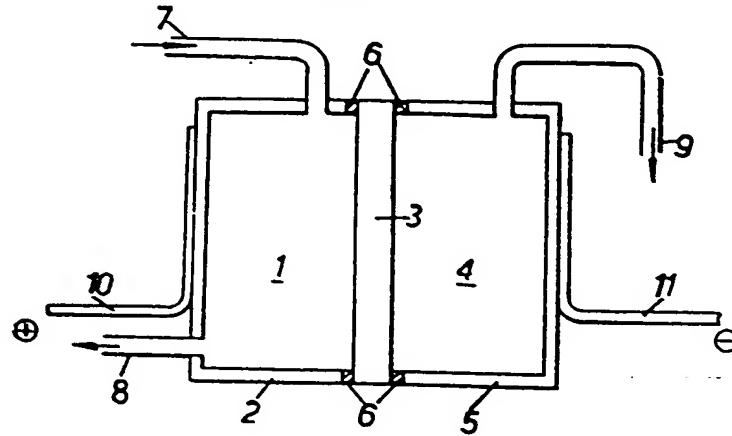


FIG.2

